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(54) Oxidation of organic compounds in water.

(57) A method of oxidizing organic compounds in aqueous solutions by using in combination ozone, hydrogen peroxide and ultraviolet radiation is provided.

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## OXIDATION OF ORGANIC COMPOUNDS IN WATER

BACKGROUND OF THE INVENTION

The present invention relates generally to detoxification of hazardous materials and more particularly, to removal of organic compounds.

At this time there is a critical national need for removing trace amounts of toxic organic compounds from groundwater, surface water and industrial waste waters without transferring these compounds to the atmosphere or to burial sites. At present, oxidation by incineration or chemical means is the only method of accomplishing true detoxification rather than mere displacement of these organic toxins into the atmosphere or to another medium.

Incineration of dilute aqueous solutions of organic components is costly due to the energy required for the evaporation of water. Moreover, incineration may cause the formation of toxic by-products, such as dioxin derivatives, in the off-gases. Chemical oxidation processes to treat contaminated water include use of such substances as for example, potassium permanganate, chlorine dioxide, chlorine, hydrogen peroxide, or ozone. Additionally, oxidation may be enhanced by using ultraviolet light (UV) in conjunction with any of these substances except permanganate.

Chemical detoxification methods are in commercial use for wastewaters and some ground waters. These methods present attendant disadvantages, however. For example, potassium permanganate produces manganese dioxide as a by-product during oxidation. Chlorine, and in some instances, chlorine dioxide, forms chlorinated organic compounds. Moreover, hydrogen peroxide plus ferrous sulfate (Fenton's reagent) produces a soluble and insoluble iron residue.

Ozonation without UV light partially oxidizes benzene derivatives to mono- and di-basic acids which are biodegradable, but does not oxidize saturated halogenated compounds. Oxidation with hydrogen peroxide and UV light is useful for oxidizing a number of organic compounds, but in many cases the rates of oxidation are significantly slower than when using UV/O<sub>3</sub>. While ozone combined with UV enhancement has been found to be cost-effective and practical for non-volatile unsaturated chlorinated hydrocarbons and a number of benzene derivatives, certain saturated chlorinated and oxygenated compounds, such as the pervasive pollutants methylene chloride and methanol, have been found to be refractory to UV-oxidation. Thus there is a long standing need for a powerful and practical method for removing a wide spectrum of toxic organic compounds from water. Such a method should provide both a highly effective and cost-effective means of detoxifying hazardous compounds. The present application fulfills these needs and provides related advantages as well.

SUMMARY OF THE INVENTION

The present invention provides a method of treating organic compounds in aqueous solutions by using in combination, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ultraviolet radiation (UV). The addition of hydrogen peroxide to the UV/ozone combination results in a greatly increased efficiency of oxidation. Such increased efficacy reflects a synergistic effect which may be related to the intermediate production of O<sub>3</sub> or HO<sub>2</sub> radicals which set in motion rapid oxidation reactions.

In a preferred embodiment, water containing halogenated hydrocarbon contaminants is exposed to ozone, hydrogen peroxide and ultraviolet radiation simultaneously. Alternatively, the water may be first exposed to UV and H<sub>2</sub>O<sub>2</sub> and subsequently O<sub>3</sub> is added thereto. The temperature of the sample may be elevated above ambient temperature.

The principal objective of the present invention is a) to provide a new and useful method for decontaminating waters containing hydrocarbons, halogenated hydrocarbons and partially oxidized hydrocarbons; b) to oxidize or partially oxidize these contaminants efficiently and economically to simple compounds such as carbon dioxide, water, and halides; and c) to oxidize less toxic partially oxidized compounds such as aldehydes, dibasic organic acids and the like, depending upon their nature, their toxicity, the source of disposal, whether a receiving water, such as a stream, river, etc., or to a biotreatment process either on site or to a publicly owned treatment works.

Other features and advantages of the present invention will become apparent from the following, more detailed description which illustrates, by way of example, the principles of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention provides a highly efficient and effective method for oxidizing organic compounds  
5 in aqueous solutions, which has particular application to oxidizing hydrocarbon contaminants in water. The  
method comprises exposing the contaminated water to H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and UV. When ground water or  
wastewater contains significant concentrations of hydrocarbon contaminants such as methylene chloride or  
methanol, these compounds are difficult to oxidize by conventional methods. With the method of the  
10 present invention, the water is exposed to H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> and UV, preferably simultaneously, or alternatively  
preliminarily with H<sub>2</sub>O<sub>2</sub> and UV followed by the addition of O<sub>3</sub>. The method is effective for oxidation of a  
wide spectrum of hydrocarbons, including halogenated and partially oxygenated hydrocarbons, whether  
aromatic or aliphatic.

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## EXAMPLE I

## OXIDATION OF METHANOL

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Samples of distilled water (Arrowhead Co., P.O. Box 2293, Los Angeles, CA 90051-0293) containing the equivalent of 200 mg methanol/liter were treated with various combinations of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and UV. For each such sample, two liters of the aqueous methanol solution was placed in an 82 x 485 mm pyrex glass cylindrical reaction vessel which was sealed at the top. UV was provided by a centrally located low pressure mercury arc lamp (G37T6VH) inside a 24 mm O.D. quartz sheath (both from Voltare Tubes, Inc.), (lamp size = 40 watts; ultraviolet output = 14.3 watts; tube diameter = 15 mm; tube material = quartz). The lamp assembly was suspended 15 mm above the bottom of the cylinder to leave room for a magnetic stirring bar.

25 Hydrogen peroxide was introduced into the reaction vessel through an opening at the top. 0.7 mL of 30% H<sub>2</sub>O<sub>2</sub> were supplied at 5 minute intervals over 20 minutes. Ozone was generated from welding grade oxygen using a Model 8341 ozonator (Matheson Gas Products Company, Lindhurst, N.Y.). 2% ozone in oxygen was bubbled in at bottom of the cylinder through a coarse frittered glass disc at a rate of 62 mg/min. The solution was stirred during the oxidation with a magnetic stirring bar. The effluent oxygen stream was passed through a solvent trap to collect materials being stripped off.

30 The rate of methanol oxidation was determined by gas-liquid chromatography (glc) using a model 340 ALP gas chromatograph manufactured by Antek Instruments, Inc., Houston, Texas. The oxidized methanol solutions were injected directly on a 6 ft. x 1/8 in. stainless steel column containing 10% Pennwalt + 4% KOH on 80/100 mesh Gas Chrom R. The column was operated isothermally at 100 °C.

35 The results of the procedures are presented in Table 1. The resulting decrease in TOC using the combination of UV, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> is greater than ten times that achieved with treatment by use of UV, H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> alone or in combinations of two.

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Table 1

Oxidation of Methanol					
<p>The methanol concentration was 200 ppm at zero time, volume of methanol solution = 2000 ml, O<sub>3</sub> concentratin in the O<sub>2</sub>-O<sub>3</sub> feed gas = 3.6%, O<sub>2</sub>-O<sub>3</sub> flow to deliver 70 mM O<sub>3</sub>/30 min = 2.2L/min.</p>					
Oxidation Conditions	No. of Runs	Time (min)	Oxidant Dose		TOC (ppm)
			O <sub>3</sub> (mM)	H <sub>2</sub> O <sub>2</sub> (mM)	
Control	1	0	--	--	75
		30	--	--	75
UV	1	0	--	--	75
		30	--	--	75
UV/H <sub>2</sub> O <sub>2</sub>	1	0	--	--	75
		30	--	70	63
H <sub>2</sub> O <sub>2</sub>	1	0	--	--	75
		30	--	70	68
O <sub>3</sub>	1	0	--	--	75
		30	70	--	47
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	1	0	--	--	75
		30	39	31	31
UV/O <sub>3</sub>	1	0	--	--	75
		30	70	--	27
UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	2	0	--	--	75
		30	39	31	1.2,±0.25
UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	1	0	--	--	75
		30	78	62	2.1

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## EXAMPLE II

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## OXIDATION OF METHYLENE CHLORIDE

45 Methylene chloride oxidation was carried out using the procedure of Example I, except that the feed samples contained 100 mg of methylene chloride/l, time of oxidation = 25 min., and each water sample to be oxidized was 1800 ml. 0.15 ml of 30% H<sub>2</sub>O<sub>2</sub> was added to the methylene chloride solution in the reaction vessel at the start. Ozone was added at a rate of 5.2 mg/min. The rate of methylene chloride oxidation was determined by hexane extraction and gas liquid chromatography using a Varian Aerograph  
50 Model 144010-00 gas chromatograph equipped with an electron capture detector (<sup>63</sup>Ni). An aliquot of the oxidized water sample diluted to contain no more than 10 ppm of methylene chloride was combined with 2 ml of high purity hexane (Burdick & Jackson, Muskegon, MI) in a 40 ml vial closed with a teflon septum lined screw cap. The contents of the vial were shaken vigorously for 1 min. and after separation of the phases one  $\mu$ l of the hexane extract was withdrawn through the teflon lined septum and injected on a 10 m  
55 x 0.53 nm i.d. wide bore capillary column coated with FSOT Superox, 1.2  $\mu$ m. The column was operated isothermally at 30 °C. The results are presented in Table 2. As in Example I, the lowest level of non-oxidized methylene chloride was obtained in those trials in which UV, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> were used in combination.

Table 2  
Oxidation of Methylene Chloride

Volume of  $\text{CH}_2\text{Cl}_2$  solution oxidized = 1800 ml;  $\text{O}_3$   
 concentration = 2%;  $\text{O}_2 - \text{O}_3$  flow to deliver 10mM  $\text{O}_3/25$   
 min = 0.5 l/min.

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	Oxidation Conditions	No. of Runs	Time (min)	Oxidant Dose	$\text{CH}_2\text{Cl}_2$ found solution (ppm)	Trap%
				$\text{O}_3$ (mM) $\text{H}_2\text{O}_2$ (mM)		
15	Control	1	0	---	100	
			10	---	100	
			25	---	100	
20	UV	1	0	---	100	
			10	---	59	
			25	---	42	
25	$\text{UV}/\text{H}_2\text{O}_2$	1	0	---	100	
			10	---	46	
			25	4.0	17	
30	$\text{H}_2\text{O}_2$	1	0	---	100	
			10	4.0	38	
			25	10	22	
35	$\text{O}_3$	1	0	---	100	
			10	4.0	44	
			25	10	18	1.2
40	$\text{O}_3/\text{H}_2\text{O}_2$	1	0	---	100	
			10	2.7	32	
			25	6.7	21	0.86
45	$\text{UV}/\text{O}_3$	2	0	---	100	
			10	4.0	36 $\pm$ 6	0.43
			25	10	16 $\pm$ 2	
50	$\text{UV}/\text{O}_3/\text{H}_2\text{O}_2$	2	0	---	100	
			10	2.7	18 $\pm$ 3.7	0.46
			25	6.7	5.2 $\pm$ 0.8	
55	$\text{UV}/\text{O}_3/\text{H}_2\text{O}_2$	1	0	---	100	
			10	5.4	19	
			25	13.4	7.6	0.35

## EXAMPLE III

## OXIDATION OF WOOD PRODUCTS MANUFACTURER WASTEWATER

Wood products manufacturer wastewater oxidation was carried out using the procedure of Example I except that the feed samples contained 29,800 Pt-Co color units and each water sample to be oxidized was 1900 ml. 1.15 ml of 30% H<sub>2</sub>O<sub>2</sub> were supplied at 5 min. intervals over 20 min. Ozone was added at a rate of 40 mg/min. The oxidized wastewater samples were diluted as needed to give the same color intensity.

The results are shown in Table 3.

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Table 3

Oxidation of a Wastewater to Remove Color Bodies from a Wood Products Manufacturer with UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> .				
Batch Operation				
	Run No.	Oxidation conditions Oxidant dose	Time	Dilution required to achieve the same color intensity
20	1	Feed UV/O <sub>3</sub> H <sub>2</sub> O <sub>2</sub> O <sub>3</sub> = 50.0 mM H <sub>2</sub> O <sub>2</sub> = 100 mM Total = 150 mM UV/O <sub>3</sub> H <sub>2</sub> O <sub>2</sub> O <sub>3</sub> = 100 mM H <sub>2</sub> O <sub>2</sub> = 21 mM Total = 121 mM UV/O <sub>3</sub> H <sub>2</sub> O <sub>2</sub> O <sub>3</sub> = 50 mM H <sub>2</sub> O <sub>2</sub> = 50 mM Total = 100 mM UV/O <sub>3</sub> O <sub>3</sub> = 100 mM	0 60 min. 60 min. 60 min.	1:99 None 1:1 1:4 1:5
25	2			
30	3			
35	4			

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## EXAMPLE IV

## OXIDATION OF CHEMICAL PLANT WASTEWATER

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Wastewater from a chemical plant containing 700 ppm of 1,4-dioxane, 1000 ppm of ethylene glycol and 1000-5000 ppm acetaldehyde was subjected to comparative oxidation using the combination of UV, H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub>. The procedure followed was that given in Example I except that the reaction time was 120 min., 35 ml of 30% of H<sub>2</sub>O<sub>2</sub> were added gradually within the first 90 min and the rate of ozone addition was 205 mg/min. The decrease in 1,4-dioxane concentration was determined by gas liquid chromatography as described in Example I, except that the glc column was operated isothermally at 140 °C.

The results are presented in Table 4. The combination of UV, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> resulted in a two to five fold reduction in dioxane over that achieved with UV and O<sub>3</sub>.

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Table 4

Oxidation with UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> on the Laboratory Bench of a Wastewater from a Chemical Plant.				
2000 ml Volume, Batch Operation				
	Run No.	Time (min)	Reaction Conditions	Dioxane found (ppm)
10	1	0	UV/O <sub>3</sub> , 124 mg O <sub>3</sub> /min	700
		60		500
		90		380
		120		260
		0	UV/O <sub>3</sub> , 205 mg O <sub>3</sub> /min	700
15	2	60		420
		90		310
		120		190
		0	UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	700
		60	205 mg O <sub>3</sub> /min	300
20	3	90	35 ml of 30% H <sub>2</sub> O <sub>2</sub>	170
		120	add H <sub>2</sub> O <sub>2</sub> within 90 min.	50
		0	UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	700
		60	124 mg O <sub>3</sub> min	320
		90	70 ml of 30% H <sub>2</sub> O <sub>2</sub>	180
25	4	120	add H <sub>2</sub> O <sub>2</sub> within 90 min.	90

## EXAMPLE V

## OXIDATION OF CHEMICAL PLANT GROUNDWATER

Comparative oxidations of groundwater containing a variety of organic compounds were performed using UV, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> and UV and O<sub>3</sub>. The procedure followed was that described in Example I except that the time was 60 min., 3.2 ml of 30% H<sub>2</sub>O<sub>2</sub> were added at the start of the oxidation and the ozone dose was 11 mg/min. The concentration of the organic compounds in the feed and in the oxidized groundwater was determined by Montgomery Laboratories, Pasadena, CA using gas liquid chromatography/mass spectrometry. The results are presented in Table 5.

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Table 5

Oxidation of Groundwater on the Laboratory Bench from a Chemical Plant with UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> .				
	Compound	Feed (ppb)	UV/O <sub>3</sub> * (ppb)	UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> ** (ppb)
Vinyl chloride	130,000	N.D.	N.D.	
Methylene chloride	13,000	N.D.	N.D.	
1,1-DCE	7,600	10	53	
1,1-DCA	7,300	N.D.	N.D.	
Trans 1,2-DCE	130,000	N.D.	62	
CHCl <sub>3</sub>	480	11	35	
1,2-DCA	95,000	5,300	6,600	
TCE	3,500	N.D.	N.D.	
PCE	200	N.D.	N.D.	
Chlorobenzene	2,900	16	N.D.	
Benzene	260	N.D.	N.D.	
Toluene	10,000	N.D.	N.D.	
Ethylbenzene	1,100	N.D.	N.D.	
Xylene	4,500	14	14	
Bromoform	----	7,900	160	
CHBrCl <sub>2</sub>	----	150	N.D.	

\* 60 min, 27.5 mM O<sub>3</sub> (= 22 mg O<sub>3</sub>/min/1.8L)\*\* 60 min, 11 mg O<sub>3</sub>/min (14 mM), 28 mM H<sub>2</sub>O<sub>2</sub> (3.2 ml 30%)

N.D. non-detectable

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## EXAMPLE VI

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## OXIDATION OF PAINT STRIPPING WASTEWATER

Paint stripping wastewater containing methylene chloride was pretreated to remove chromate ions and paint chips. The pretreatment consisted of using sodium meta bisulfite to reduce the chromate ion to Cr<sup>+</sup><sup>4+</sup> and then adding sodium hydroxide and a anionic polymer solution to form a rapidly settled Cr(OH)<sub>3</sub> precipitate. Three ml of 0.76% Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> were added to 100 ml of the wastewater adjusted to pH 4. After 30 min add NaOH to pH 8.5 and then a anionic polymer solution to give 0.5 ppm of the anionic polymer. The precipitated Cr(OH)<sub>3</sub> was filtered off and the filtrate oxidized with UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> according to the procedure given in Example 1 except that samples were obtained at 15 min. intervals. The total time for the oxidation was 60 min., the volume of the wastewater was 1800 ml, the total H<sub>2</sub>O<sub>2</sub> dose was 4.7 ml of 30% H<sub>2</sub>O<sub>2</sub>, and the ozone dose was 21.5 mg/min. The methylene chloride decrease was measured as described Example II.

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Table 6

Bench Test Results on Pretreated Paint Stripping Wastewater		
Methylene chloride vs. reaction time		
	Time (min)	Methylene Chloride (ppm)
5	0	70
10	15	2.1
15	30	0.49
20	45	0.02
25	60	N.D.
30	N.D. non-detectable Conditions: O <sub>3</sub> /O <sub>2</sub> flow = 0.75 L/min @2% (wt) O <sub>3</sub> , 1.8 L batch of pretreated paint stripping wastewater, H <sub>2</sub> O <sub>2</sub> dose = 2.6 ml @ 30%/l liter wastewater, 14.9 mM O <sub>3</sub> /12.7 mM H <sub>2</sub> O <sub>2</sub> .	

Although the invention has been described with reference to the presently-performed embodiment, it should be understood that various modifications can be made without departing from the spirit of the invention. Accordingly, the invention is limited only by the following claims.

### Claims

1. A method of oxidizing halogenated and/or partially oxygenated hydrocarbon constituents in aqueous solution comprising simultaneously exposing said aqueous solution to an amount of ozone, hydrogen peroxide and ultraviolet radiation sufficient to substantially reduce said constituents in the solution.
2. The method of claim 1 wherein said aqueous solution is ground water.
3. The method of claim 1 or 2 wherein said aqueous solution is industrial waste water.
4. The method of any of the preceding claims wherein said aqueous solution is drinking water.
5. The method of any of the preceding claims wherein said organic constituents are methylene chloride.
- 45 6. The method of any of the preceding claims wherein said method further comprises elevating the temperature of said aqueous solution during exposure to said ozone, hydrogen peroxide and ultraviolet light.
7. The method of any of the preceding claims wherein said organic constituents are methanol.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 512 900 (G.J. MACUR et al.) * Column 1, lines 30-50; column 3, lines 17-27,62-68; claims 1,8,11 * ---	1,3,6	C 02 F 1/72 C 02 F 1/32 C 02 F 1/78
X	FR-A-2 303 766 (SOCIETE NATIONALE DES PETROLES D'AQUITAINE) * Page 2, lines 3-24; page 3, lines 5-16 *	1,3	
X	DE-A-2 642 752 (H. HANSCHMANN) * Pages 1-3; claim 1 *	1,4	
A	FR-A-2 378 722 (GENERAL ELECTRIC) * Page 1, lines 1-13; page 9 *	1-7	
			TECHNICAL FIELDS SEARCHED (Int. CL5)
			C 02 F
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	17-07-1989	VAN AKOLEYEN H. T. M.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	